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NATIONAL WATER QUALITY NETWORK. REPORT
ON ANALYTICAL REFERENCE SAMPLE TYPE I,
BD-5

Robert A. Taft Sanitary Engineering Center
Cincinnati, Ohio

1960

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NATIONAL WATER QUALITY NETWORK

**report on
analytical reference
sample**

**TYPE I, BD-5
1960**

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**U. S. DEPARTMENT OF
HEALTH, EDUCATION, AND WELFARE**
Public Health Service
Robert A. Teft Sanitary Engineering Center
Cincinnati, Ohio

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Participants in Study of Type I, BD-5

(Distributed May 31, 1960)

Louisiana Regional Laboratory
Alexandria, Louisiana

Massachusetts State Health Department
Amherst, Massachusetts

Baltimore Water Department
Baltimore, Maryland

Bismarck Water Department
Bismarck, North Dakota

Public Health Laboratory
Bismarck, North Dakota

Boulder City Water Department
Boulder City, Nevada

Brownsville Water Department
Brownsville, Texas

Erie County Health Department
Buffalo, New York

Burlington Water Department
Burlington, Iowa

Cairo Water Company
Cairo, Illinois

Crown Zellerback Corporation
Camas, Washington

Missouri Utilities Company
Cape Girardeau, Missouri

City Water Company
Chattanooga, Tennessee

Tennessee Valley Authority
Stream Pollution Laboratory
Chattanooga, Tennessee

Cincinnati Water Department
Cincinnati, Ohio

Columbus Water Department
Columbus, Georgia

Denison Water Department
Denison, Texas

Detroit Water Department
Detroit, Michigan

Duluth Water Department
Duluth, Minnesota

East St. Louis Water Company
East St. Louis, Illinois

El Paso Water Department
El Paso, Texas

Evansville Water Department
Evansville, Indiana

St. Joan County Health Department
Farmington, New Mexico

Grand Junction Water Department
Grand Junction, Colorado

Hagerstown Water Department
Hagerstown, Maryland

Huntington Water Corporation
Huntington, West Virginia

Mississippi State Health Dept. Lab.
Jackson, Mississippi

Kansas City Water Department
Kansas City, Kansas

Laredo Water Department
Laredo, Texas

Arkansas State Pollution Control
Commission
Little Rock, Arkansas

Pennsylvania Power & Light
Martins Creek, Pennsylvania

Memphis Water Department
Memphis, Tennessee

Louisiana State Health Dept. Lab.
New Orleans, Louisiana

Metropolitan Utilities District
Omaha, Nebraska

Bureau of Reclamation
Page, Arizona

Pasco Water Department
Pasco, Washington

Peoria Water Company
Peoria, Illinois

Philadelphia Water Dept. - Belmont
Philadelphia, Pennsylvania

Philadelphia Water Dept. - Torresdale
Philadelphia, Pennsylvania

Washington State University
Pullman, Washington

St. Louis Water Department
St. Louis, Missouri

St. Joseph Water Company
St. Joseph, Missouri

Minneapolis-St. Paul Sanitary District
St. Paul, Minnesota

Sault Ste. Marie Water Department
Sault Ste. Marie, Michigan

Chatham County Health Department
Savannah, Georgia

Union Bag-Camp Paper Company
Savannah, Georgia

Montana-Dakota Utilities
Sidney, Montana

St. Louis County Water Company
University City, Missouri

Dalecarlia Filtration Plant
Washington, D.C.

Weiser Water Department
Weiser, Idaho

Aluminum Company of America
Wenatchee, Washington

Williston Water Department
Williston, North Dakota

Yankton Water Department
Yankton, South Dakota

Arizona Water Company
Yuma, Arizona

Unidentified - I

Unidentified - II

INTRODUCTION

Much of the physical and chemical data accumulated by the PHS National Water Quality Network are the result of the cooperative efforts of many laboratories located at or near the sampling sites. Because these analyses originate from so many different sources, it is essential that they be comparable as to accuracy. The reference sample technique is a mechanism by which this objective can be achieved. Reference samples are being submitted periodically to each of the cooperating laboratories to insure continued accuracy of the data submitted.

REPORT ON THE ANALYTICAL REFERENCE SAMPLES

TYPE I, BD-5

Sample Type I, BD-5 is the fifth in a series of standard samples representative of the mineral analyses being reported to the network. Sixty-six laboratories received this sample and 56 have reported in time to have their results included in this report. Two of the reports submitted were unidentified as to origin. Most laboratories have little or no difficulty in performing these examinations, as confirmed by the general excellence of the reported results.

The individual analyses are presented in Table II and the bar graphs. The dotted lines on the graphs represent limits of accuracy for this sample which are acceptable to the program. The selection of these limits was influenced by the accuracy with which each test can be performed, as determined by "Standard Methods" as well as the needs of the program. In most cases, those laboratories falling outside the acceptable range were notified immediately and requested to review the procedures used in order to determine the reasons for the discrepancies.

It is strongly urged that all cooperating laboratories furnish comments on the analytical methods used. A complete log of pertinent details, difficulties, modifications, sources of error, and other factors affecting the precision and accuracy of the analytical procedures would be extremely valuable in the development of simpler and more accurate analytical procedures. This report may also be useful as a means of self-evaluation by each of the participating agencies. Assistance on laboratory procedures is available to the cooperating laboratories from the Public Health Service, through its Regional Offices or the Sanitary Engineering Center.

DISCUSSION OF RESULTS

Statistical comparisons in this report were developed from the deviations from known quantities added to the sample. The range of deviations considered acceptable to the program were based on the precision and accuracy values as presented in "Standard Methods" for the various tests involved. Table I, below, is a summary of the expected accuracy for the various tests, from "Standard Methods", and the ranges acceptable for the Water Quality Network for this reference sample.

Laboratories reporting values outside the range of acceptability should investigate their procedures for sources of error. Have standard solutions been checked recently? Are the reagents too old? Are sample sizes adequate for maximum accuracy? How carefully are weighings being made? Are standard curves being checked frequently? Although most of these tests are simple and "routine", a thorough review of the details in each procedure may disclose errors which have become habitual and escape unnoticed during routine operations.

TABLE I
Acceptable Limits of Accuracy

	Standard Methods	Water Quality Program
Chloride 100 ml sample	± 1.0 mg/l	± 2.0 mg/l
Sulfate Turbidimetric	$\pm 10\%$	$\pm 10\%$
Alkalinity 50 ml sample	± 2.0 mg/l	± 4.0 mg/l
T.D.S. 200 ml sample	± 10 mg/l	± 20 mg/l
Hardness 50 ml sample	± 2 mg/l	± 4.0 mg/l
pH	± 0.1 unit	± 0.2 unit
Turbidity	-	± 44 units

The Tenth Edition of "Standard Methods" gives the expected precision and accuracy for most tests, within the range of concentration normally encountered in water analysis. These "standards of accuracy" should be attainable by

most laboratories performing these routine examinations. The additional errors, allowable for the Network Program, are intended only as a guide to the cooperating laboratories and are not to be considered as the ultimate goal in the achievement of laboratory accuracy.

CHLORIDE - 52 mg/1

Although several methods are available for this determination, 31 laboratories used the Mohr procedure. The most frequent criticism of this method is the obscurity of the real endpoint due to the presence of the Silver Chloride precipitate. A frequent, but minor error is failure to correct for the indicator blank. The use of a yellow light aids in detecting the endpoint. The chief precaution to be observed in this determination, as in any volumetric procedure, is standardization of reagents. Twenty-five of the fifty laboratories reporting this analysis fell within ± 2 mg/1 of the known value. Six additional laboratories fell within ± 3 mg/1 and sixteen of the reported results were within ± 1 mg/1 of the known value. Most laboratories should have no difficulty in performing the chloride determination within the limits of precision.

SULFATE - 75 mg/1

Thirty of the 37 laboratories reporting this analysis fell within $\pm 10\%$ of the known value. Only three laboratories failed to come within $\pm 20\%$. Of these, one reported using the Tetrahydroxyquinone (THQ) procedure; one reported using the turbidimetric procedure and a colorimeter; and the third reported using the gravimetric procedure.

At higher sulfate concentrations, the gravimetric procedure is considered to be the more accurate, but at the concentration present in this sample the turbidimetric procedure appears to be equally satisfactory. The turbidimetric procedure has the advantages of being less time consuming and more simple to perform.

On this particular sample, using either turbidimetric or gravimetric procedures, it was necessary to remove the turbidity prior to sulfate precipitation. If this operation was not properly performed, a high result would be obtained. The usual precautions of washing and drying precipitates also had to be observed to obtain good results on the gravimetric procedure.

TOTAL DISSOLVED SOLIDS - 507 mg/l

In the performance of the Total Dissolved Solids determination, no difficulties should normally be encountered. A measured volume of turbidity-free sample is placed in a dish, evaporated to dryness and weighed. Two precautions must be observed: (1) the turbidity must be completely removed, and (2) the sample must be taken to dryness at 103 - 105°C. Incomplete drying allows excessive amounts of water to be included in the final weighing which, along with turbidity particles, will cause high results. A third precaution, also related to drying, must be exercised. If the drying temperature is too high, certain materials, such as carbonates, bicarbonates, or chlorides, may be partially volatilized and the result will be too low. For these reasons the precautions, while simple, must be strictly observed. The size of sample taken for this test will influence its precision considerably, particularly with waters of low solids content. To achieve a satisfactory result the sample size should be large enough to produce a residue weighing not less than 25 mg in order that the precision of the weighing fall within the acceptable range.

Of the 39 laboratories reporting this determination, 22 fell within the ± 20 mg/l range and only 7 fell beyond the ± 40 mg/l range.

Grossly erroneous results on the high side are probably due to incomplete removal of turbidity particles. A very retentive filter, preferably a millipore, is required for complete removal of turbidity.

ALKALINITY - 82 mg/l (as CaCO_3)

This procedure allows a choice of indicators or electrometric measurement for the detection of the endpoint. Of the 55 laboratories reporting this analysis, 20 used methyl orange indicator; 6 used methyl purple; 3 used mixed indicator; and 7 used a pH meter. The other laboratories did not report the method used. Thirty-eight results were within ± 4 mg/l and only six were beyond ± 8 mg/l. Of these, the two highest might contain arithmetical errors such as a misplaced decimal point or an incorrect dilution factor. It is of interest that of the seven laboratories using an electrometric endpoint, five obtained results within ± 1 mg/l of the known value.

HARDNESS - 144 mg/l

All laboratories employed some modification of the EDTA titration procedure, with one exception which used the soap procedure and obtained a result of only one half the known value. Fifteen of the 54 laboratory results fell within ± 4 mg/l of the concentration added to the sample. Sixteen additional laboratories

fell within ± 8 mg/l. This titration seldom presents any difficulty as the endpoint is easy to detect, provided that the indicator, Eriochrome Black T, is in good condition. This may be assured by using the indicator in dry form, mixed with sodium chloride. Usually, errors are due to improperly standardized reagent, miscalculation, or faulty indicator. This sample was well buffered, which may have caused some difficulty if the analyst failed to adjust the pH properly before performing the titration.

HYDROGEN ION CONCENTRATION (pH) - 7.5

This component of the sample was prepared from a Clark and Lubs buffer and the pH was verified at the SEC by averaging the results from three carefully standardized pH meters. Of the 55 laboratories reporting this analysis, 43 fell within ± 0.2 units of the known value. More than half of the results were within ± 0.1 units of the true value. Thirty-eight laboratories reported using a pH meter, six specified the Hellige apparatus, three used a colorimeter, and seven used indicator without specifying the method of comparison.

TURBIDITY - 220 Jackson units

The turbidity value assigned to this sample was obtained by a series of readings on the Jackson Candle Turbidimeter following a period of aging after the sample was prepared. This value persisted for a period of two months and a recheck after four months showed a reduction to 200 units which may have been due to agglomeration of the particles.

Of the 51 laboratories reporting this analysis, half fell within ± 44 units of the initial known value, and 37 were within ± 44 units of the final value. The deviations were on the low side, which suggests the possibility that insufficient shaking of the sample might be the cause of the error. Another source of error may be the conversion to Jackson units when instruments other than the Jackson Candle turbidimeter are used. Twenty-eight laboratories reported using the Jackson Candle apparatus, ten used the Hellige and five used a colorimeter. It is of interest to note that the seven lowest results were obtained by the use of equipment other than the Jackson Candle turbidimeter.

TABLE II - SUMMARY OF RESULTS
ANALYTICAL REFERENCE SAMPLE TYPE I, BD-5

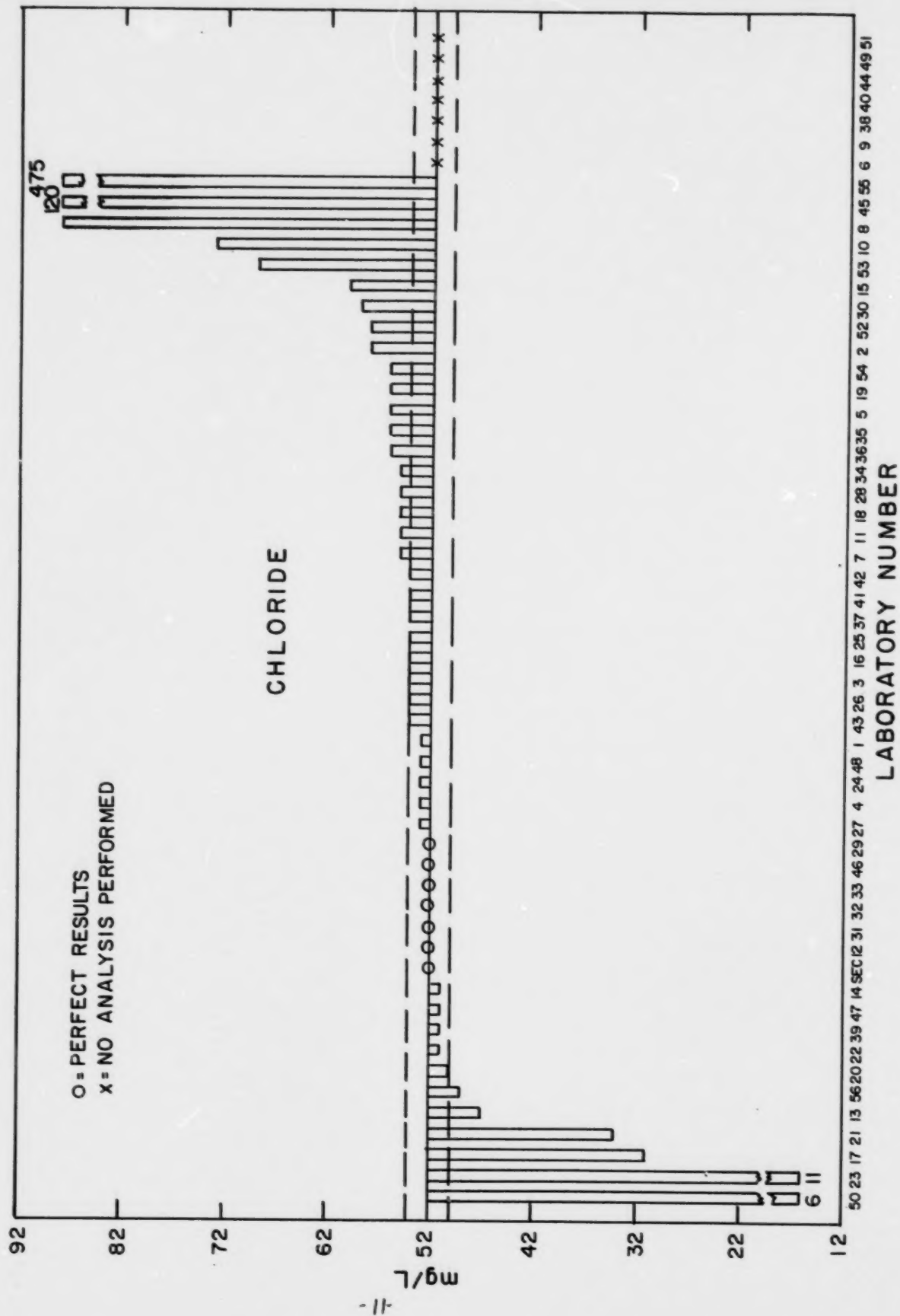
Analyses Performed	Chloride	Sulfate	T.D.S.	Alkalinity	Hardness	pH	Turbidity
Amount Added	52 mg/l	75 mg/l	507 mg/l	82 mg/l	144 mg/l	7.5	220
Lab #	Average Amount Reported by Each Lab						
SEC	52	76	511	83	143	7.5	220
1	53	72	499	78	149	7.4	170
2	58	22	381	86	148	7.3	176
3	54	--	---	89	147	7.3	180
4	53	--	---	79	145	7.3	143
5	56	--	---	80	150	7.5	---
6	--	--	---	98	150	7.4	180
7	55	--	---	90	152	7.4	135
8	88	33	423	82	133	7.4	148
9	--	84	488	--	---	---	---
10	73	--	---	85	143	7.3	210
11	55	75	482	81	149	7.3	171
12	52	--	---	92	160	7.2	82
13	47	85 ^{cc}	---	90	149	7.4	111
14	51	70	504	80	152	7.5	190
15	60	80	473	84	155	7.5	155
16	54	67	500	82	158	7.3	170
17	31	--	---	88	145	7.3	170

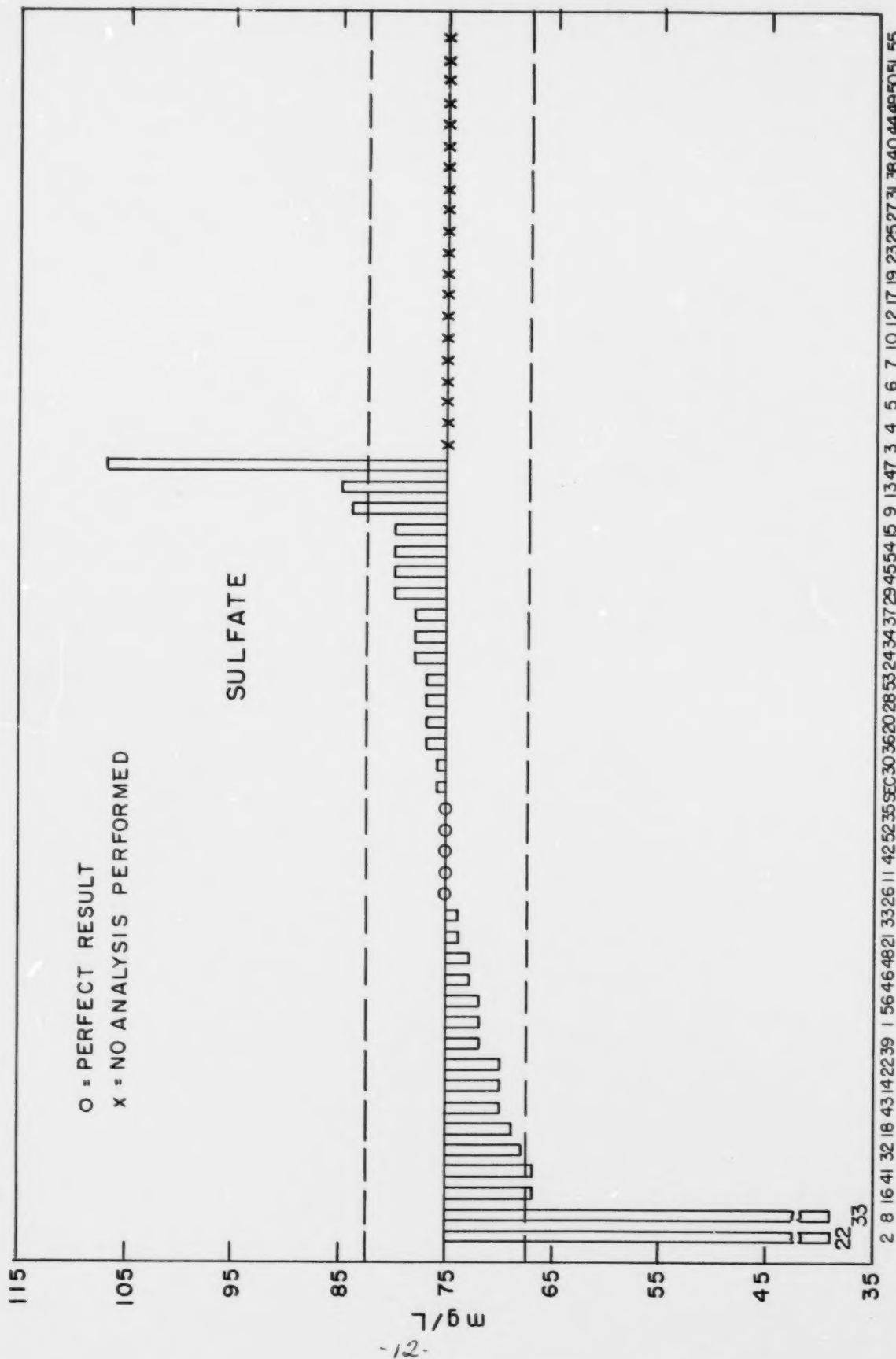
Analyses Performed							
Chloride	Sulfate	T.D.S.	Alkalinity	Hardness	pH	Turbidity	
Amount Added	52 mg/l	75 mg/l	507 mg/l	82 mg/l	144 mg/l	7.5	220
Lab #	Average Amount Reported by Each Lab						
18	55	69	489	83	163	7.5	162
19	56	--	---	82	133	7.3	203
20	50	77	499	83	153	7.4	180
21	34	74	524	66	150	7.4	192
22	51	70	518	74	149	7.6	214
23	11	--	---	85	176	7.2	54
24	53	78	481	81	154	7.3	225
25	54	--	527	140	156	7.7	210
26	54	75	497	83	78	7.2	183
27	53	--	---	88	152	7.2	13
28	55	77	518	77	157	6.9	54
29	52	80	885	--	---	---	---
30	59	76	486	86	147	7.4	200
31	52	--	---	80	139	7.4	200
32	52	68	400	78	131	7.4	168
33	52	74	479	76	137	7.5	153
34	55	78	515	82	169	7.5	196
35	56	75	485	84	146	7.5	220
36	56	77	444	82	144	7.4	187
37	54	78	520	89	150	7.2	---
38	--	--	---	78	120	8.6	210

Analyses Performed	Chloride	Sulfate	T.D.S.	Alkalinity	Hardness	pH	Turbidity
Amount Added	52 mg/l	75 mg/l	507 mg/l	82 mg/l	144 mg/l	7.5	220
Lab #	Average Amount Reported by Each Lab						
39	51	72	453	83	152	7.6	180
40	--	--	---	81	142	7.5	---
41	54	67	511	85	117	7.4	200
42	54	75	500	80	150	6.9	150
43	54	70	497	81	155	7.5	150
44	--	--	494	105	75	7.4	40
45	120	80	498	81	153	7.4	143
46	52	73	495	81	153	7.4	173
47	51	107	481	83	147	7.3	160
48	53	73	514	79	147	7.4	175
49	--	--	628	83	101	7.2	198
50	6	--	---	88	142	7.3	214
51	--	--	---	82	---	7.4	---
52	58	75	475	82	147	7.4	190
53	69	77	479	85	152	7.2	171
54	56	80	478	76	142	7.2	180
55	475	--	---	704	124	7.3	170
56	49	72	527	83	154	7.2	187
mean	*54	73	502	**83	144	7.4	167
median	54	75	497	83	149	7.4	176

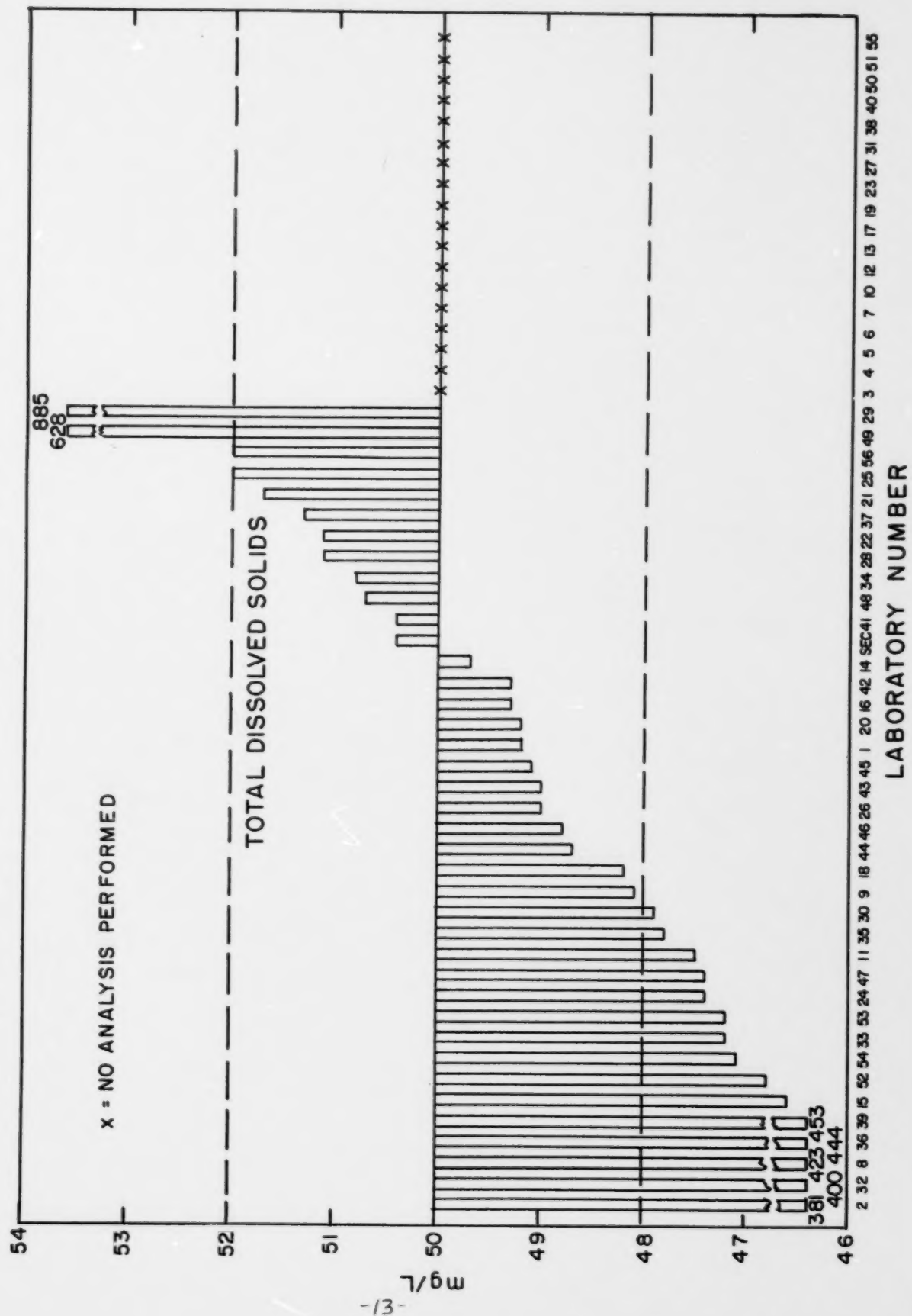
* minus the two highest and two lowest results

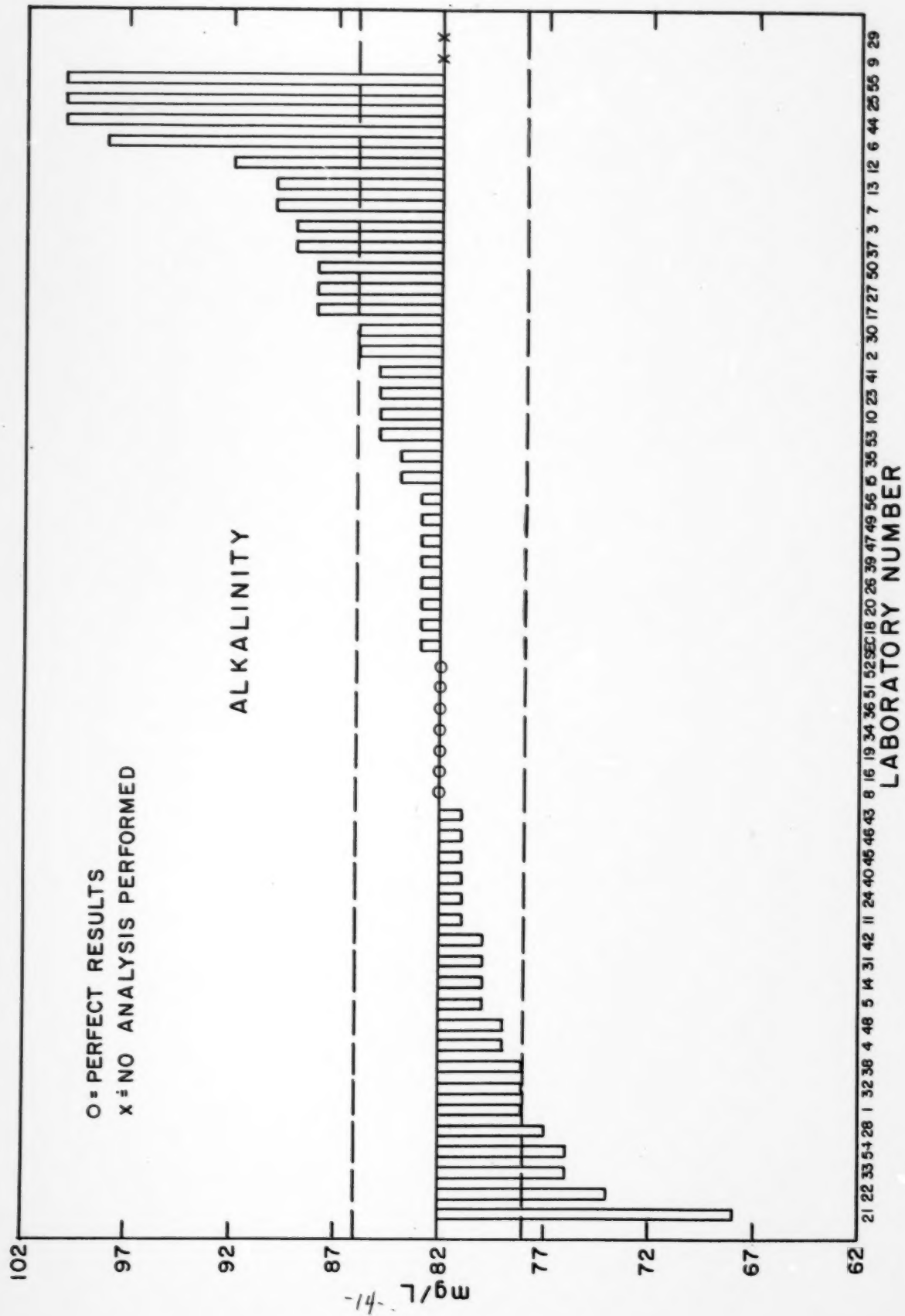
** minus the three highest results

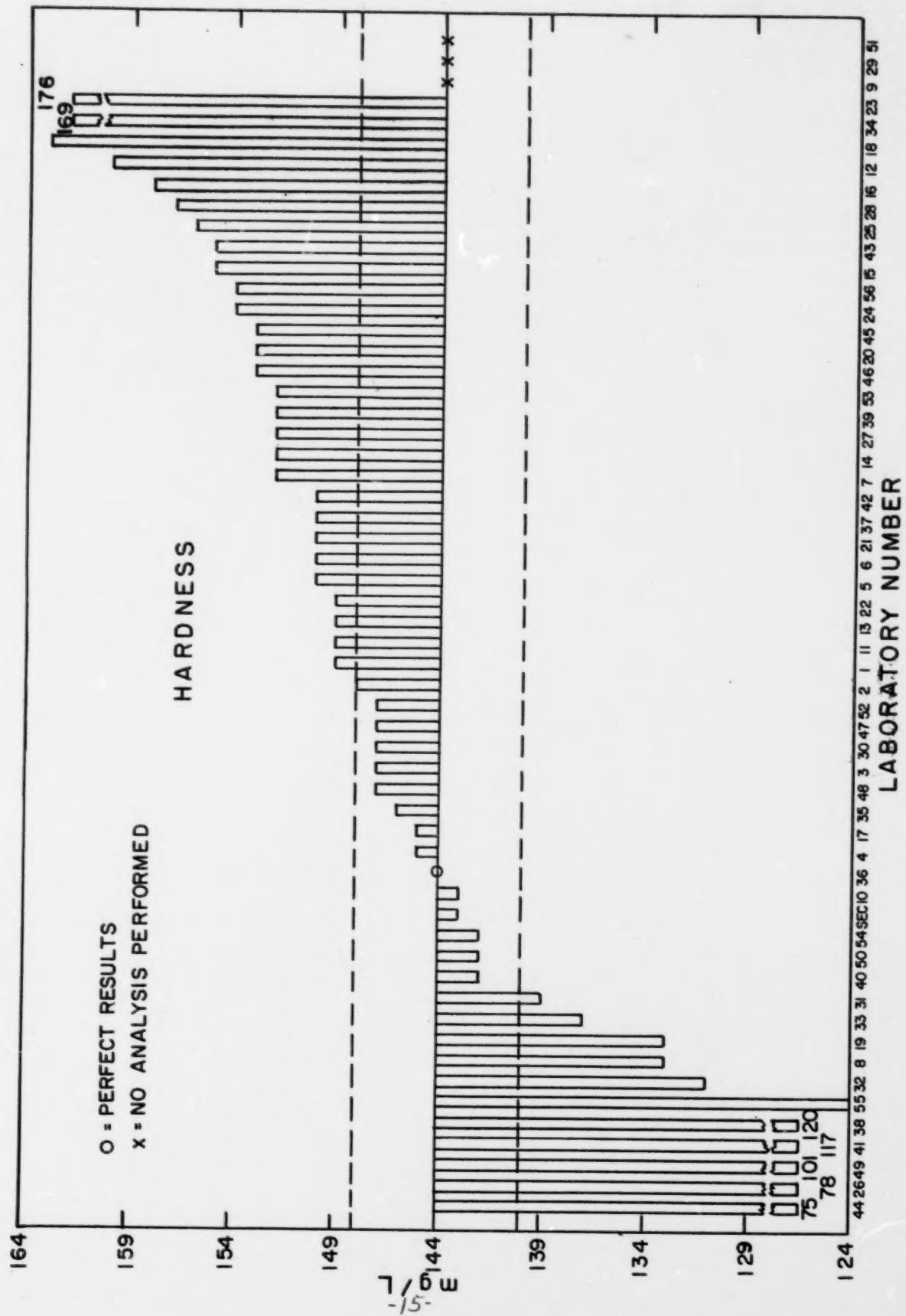


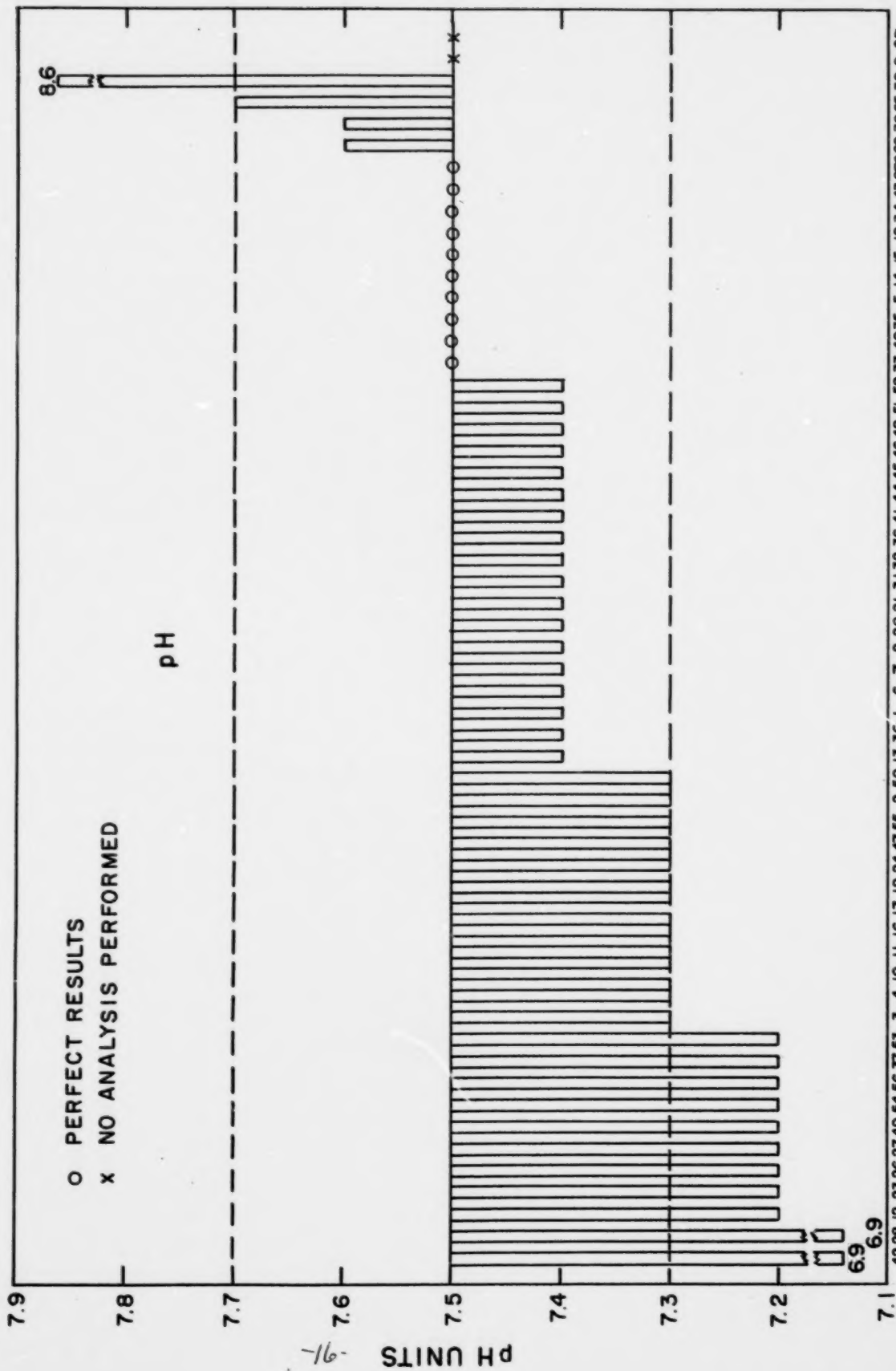


LABORATORY NUMBER









LABORATORY NUMBER

42 28 12 23 26 27 49 54 56 37 53 3 4 10 11 16 17 19 24 47 55 2 50 13 30 1 6 7 8 20 21 31 32 36 41 44 45 46 48 51 52 33 40 35 5 14 15 18 34 43 SEC 22 39 25 38 9 29

